



Evaluation of nickel deposition by electrochemical impedance spectroscopy

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Abstract

Electrochemical impedance spectroscopy was used to characterize the deposition of nickel from unbuffered acid sulfate electrolytes, from which a wide range of deposit morphologies and current efficiencies are possible. The operating parameters were in the range of 40 to 60 g L⁻¹ Ni²⁺, 40 to 60 °C, and the pH from 2.0 to 3.5. The resulting impedance spectra for nickel deposition at 20 mA cm⁻² consisted of one or two characteristic loops whose frequency and capacitance were dependent upon the electrowinning conditions and indicative of the resultant deposit morphology. A single high frequency capacitive loop, on the order of 1 kHz, correlated to good quality deposits which were flat, smooth and ductile. The presence of a low frequency loop, on the order of a few hertz, indicated a degraded deposit morphology which showed localized dark, glassy areas and were cracked, curled and brittle. The second loop may be associated with a diffusion controlled component in the reaction mechanism. Deposits of intermediate quality had impedance spectra consisting of both type loops. No apparent trend between the impedance spectra and the deposit current efficiency was determined, but a correlation with deposit quality was clearly established.

1. Introduction

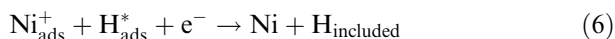
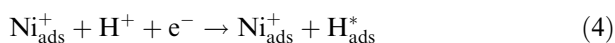
Previous research showed that the addition of a modifier such as boric acid allowed electrowinning of high quality nickel deposits under a broad range of electrolyte parameters. In the absence of additives, producing good nickel deposits from an acid-sulfate electrolyte was dependent on electrolyte parameters such as nickel concentration, temperature and pH. High quality deposits, with uniformly dense and smooth surfaces and good ductility, could only be obtained under certain conditions. High nickel concentration and electrolyte temperature, or low electrolyte pH were found to be most favorable. The inorganic additives showed little influence on the current efficiency. Increasing either the nickel concentration or electrolyte temperature improved the current efficiency, while decreasing the pH significantly reduced the current efficiency [1]. Thus, the additives and operating parameters have a complex relationship in terms of their influence on the deposition mechanism.

The mechanism of Ni²⁺ reduction from acid sulfate solutions has been extensively studied by Epelboin et al., using Watt's electrolytes [2–5]. It is generally acknowledged that the electrocrystallization of the Ni²⁺ ion will occur in several steps. It was suggested that

there were two successive faradic reactions, the first involving the formation of Ni_{ads}⁺ followed by subsequent reduction to Ni. However, H⁺ is reduced to H_{ads} in the presence of freshly deposited nickel, which strongly bonds to the electrode surface and inhibits reduction. The relative surface area decreases and the true local current density increases, causing deposit darkening and poor deposit properties. Furthermore, the localized concentration of hydroxide ions at the surface will increase, resulting in the formation of a green precipitate if the solubility of nickel hydroxide is exceeded [6, 7].

Most of the studies conducted to date point to a complex relationship between the nature and presence of inhibiting species and the reduction of nickel and hydrogen. For example, increasing the nickel concentration would increase its activity, favoring equilibrium deposition. The higher nickel deposition flux decreases the partial current of hydrogen reduction, preventing an increase in the surface pH [8]. The metal ion activity also increases with increasing electrolyte temperature. A higher electrolyte temperature not only increases the solubility of nickel hydroxide, but also increases the mobility of electrolyte components, such as Ni²⁺ and H⁺ [9]. Decreasing the bulk pH increases the diffusion gradient, decreasing the surface pH, but also *enhances* hydrogen evolution and decreases the current efficiency.

Complex reaction mechanisms such as these have been analysed by means of electrochemical impedance spectroscopy, EIS, which evaluates the rate-controlling reactions and their velocity or relaxation rate [10]. The magnitude of the charge transfer resistance is an indicator of the ease of the reaction. Similarly, high reduction rate reactions appear at high frequencies on the impedance spectra, while adsorbed films appear at lower frequencies. It has been suggested that capacitive features at a few mHz arise from H_{ads}^* and inductive features which appeared at a few Hz were the result of the relaxation or lessening of the cathode coverage by an inhibiting species such as $NiOH_{ads}$ [2–5]. From a pH 2–4 electrolyte, the following deposition mechanisms were suggested [4, 11, 12]:



Most of the literature available relating impedance data to nickel deposition has used electrolytes with high buffer contents under conditions substantially different than those typically found for unbuffered acid sulfate electrolytes in electrowinning operations. Epelboin et al. [2, 3] measured the impedance spectra under either low-current density ($<10 \text{ mA cm}^{-2}$) or high current density ($>100 \text{ mA cm}^{-2}$) conditions, while the current density for electrowinning operations is usually 20 to 22 mA cm^{-2} . No specific mention of resultant deposit quality was made, presumably because a Watt's electrolyte at 30 to 50°C was used. Such an electrolyte contains approximately 40 g L^{-1} boric acid, indicating that all the deposits would be of good quality. In separate studies, Valles et al. [6] produced poor quality deposits from chloride electrolytes but no impedance data, correlating or otherwise, were presented.

In some respects, nickel deposition from an acid sulfate electrolyte may be similar to zinc deposition in electrowinning systems. The proposed reaction involves a two-step discharge, with Zn^{2+} ions catalyzed by active Zn^* sites, but inhibited by adsorbed hydrogen. Impurities such as Ge^{4+} , Sb^{3+} and Ni^{2+} are all detrimental to the zinc cathode quality and current efficiency. The adsorbed impurities disrupt the double-layer film formed by zinc species, which enhances the evolution of hydrogen and lowers current efficiency. This results in an undesirable morphology characterized by localized zinc dissolution, a condition that also decreases current efficiency. Impedance plots showed the appearance of

representative, capacitive loops in the presence of relatively low concentrations of Ge^{4+} and Ni^{2+} , and in the presence of Sb^{3+} , the charge transfer resistance of the hydrogen reaction was significantly decreased [13–15].

In the case of nickel electrowinning, a low-frequency loop indicative of strongly adsorbed species, which impedes or modifies the nickel deposition mechanism, could explain the decrease in deposit quality. Conversely, factors which reduce the presence of an inhibiting species at the surface would improve the deposit quality and remove the low-frequency loop on the impedance spectra.

The purpose of this research was to examine the effect of electrolyte parameters and additives on both deposit morphology and electrochemical behavior. Short time deposits were used for characterizing the physical properties and deposit morphology and these were correlated with EIS tests made at an equivalent current density of 20 mA cm^{-2} , using an electrodeposited nickel surface.

2. Experimental details

2.1. Cathode blanks

Cathode blanks were 316L stainless steel sheets 8 cm long, 2.5 cm wide, and 1 mm thick. The working electrode was prepared by acetone cleaning in an ultrasonic bath for five minutes, rinsing with deionized water, and drying in an air stream. Each electrode was taped to give an area of 0.5 cm^2 for deposition.

2.2. Solution preparation

Pure, synthetic electrolytes were prepared from Fisher certified grade nickel sulfate hexahydrate ($NiSO_4 \cdot 6H_2O$) and anhydrous sodium sulfate (Na_2SO_4), to give the desired Ni^{2+} and sodium sulfate concentration. Fisher certified grade boric acid was added when necessary. The final room temperature electrolyte pH was adjusted using reagent grade sulfuric acid.

2.3. Galvanostatic deposition

The nickel deposits were made galvanostatically using electrolytes with various compositions. The standard conditions for the experiments were three hours deposition time at 20 mA cm^{-2} , and an unstirred electrolyte at 40 or 60°C . The Pb–Ca–Ag alloy anode was placed inside diaphragm material to prevent extensive mixing.

2.4. Deposit examination

The nickel deposits were examined with a light microscope and a scanning electron microscope to characterize

the morphological features of the deposits. The current efficiency was calculated by comparing the actual mass of the deposit to the theoretical mass calculated by Faraday's laws.

2.5. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) data were acquired using a Solartron 1255 HF frequency response analyser in the frequency range from 100 kHz to 10^{-2} Hz using a sinusoidal signal with a 10 mV a.c. amplitude. An Hg/Hg₂SO₄ (saturated K₂SO₄) reference electrode (+0.656 V vs SHE) and platinum counter electrode were used. The working electrode was allowed to stabilize galvanostatically for 10 min at 20 mA cm⁻² in the test electrolyte, after which time the deposition potential was measured and the impedance tests were initiated. The charge transfer resistance, R_{ct} , and the reaction velocity, ω_{max} , were measured from the impedance spectra and used to calculate the magnitude of the capacitive elements.

3. Results and discussion

3.1. Deposit morphology

Previous research identified the significance of the electrolyte nickel concentration, pH and temperature on the resultant morphology and current efficiency of the nickel cathode. It was found that high quality nickel deposits, those which were fully dense, flat, smooth and ductile enough to undergo a series of repeated bends without breaking, could be produced from an electrolyte containing 10 g L⁻¹ H₃BO₃, 40 g L⁻¹ Ni²⁺ and 150 g L⁻¹ sodium sulfate at pH 2.5 and 40 °C, as seen in Figure 1(a). In the absence of 10 g L⁻¹ H₃BO₃ the deposit was brittle and consisted of two phases; the desired nickel phase and a dark, glassy phase, as seen in Figure 1(b).

In the absence of boric acid, the electrolyte nickel concentration, pH, and temperature had a significant influence on the deposit morphology. Increasing the nickel concentration to 60 g L⁻¹ Ni²⁺ increased the current efficiency to 91% and improved the quality of the morphology considerably, but the deposit was still somewhat degraded and slightly brittle. Decreasing the electrolyte pH to 2.0 gave a good quality deposit, similar to that achieved with 10 g L⁻¹ H₃BO₃, but decreased the current efficiency by approximately 15%. Similarly, increasing the pH to 3.5 severely degraded the deposit morphology, causing extensive cracking, curling and darkening of the deposit, as seen in Figure 1(c). Increasing the temperature to 60 °C was very effective at raising the deposit current efficiency and improving the deposit morphology, resulting in a deposit similar to that obtained with 10 g L⁻¹ H₃BO₃ in Figure 1(a). Stirring the electrolyte resulted in a similar improvement in the deposit morphology, but decreased the current efficiency by approximately 6%.

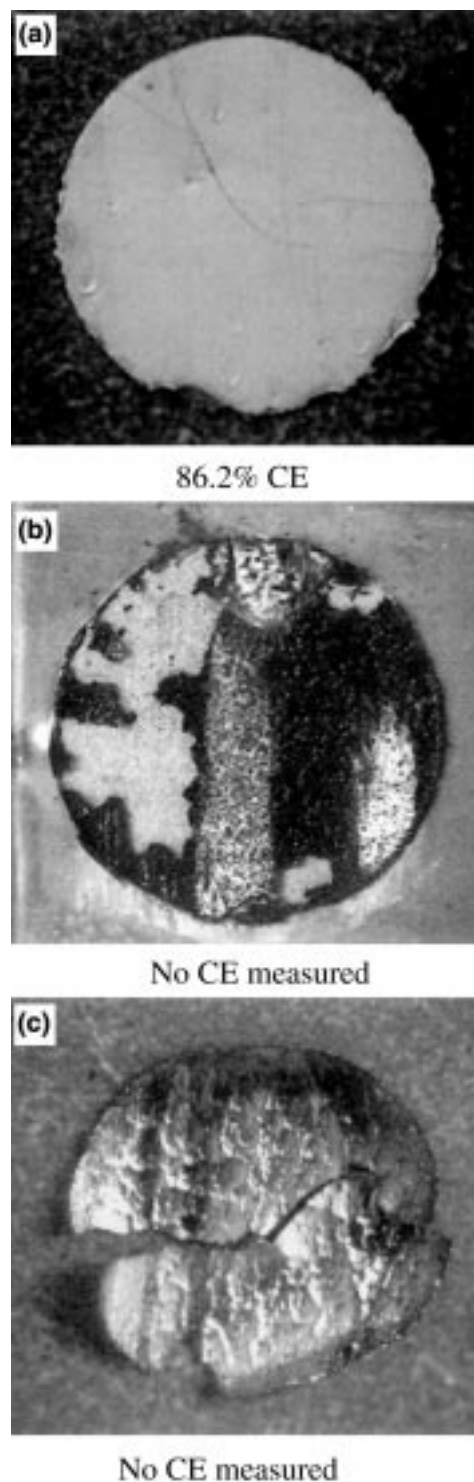


Fig. 1. Nickel deposits from synthetic electrolyte containing 40 g L⁻¹ Ni²⁺ and 150 g L⁻¹ sodium sulfate at 40 °C, no stir, Pb anode, thick stainless steel cathode: (a) 10 g L⁻¹ H₃BO₃ at pH 2.5, (b) pure at pH 2.5, (c) pure at pH 3.5.

3.2. Electrochemical impedance spectroscopy

Since the morphology and quality of nickel deposits made under a variety of conditions varied so substantially, impedance spectroscopy tests were conducted to determine if systematic variations in the electrochemical reactions occurred with changes in the operating

parameters. All the impedance spectra for nickel deposition generated during this study were characterized by the presence of one or two loops of significantly different magnitudes, depending on the operating parameters. In particular, the magnitude of the capacitance of the two varied substantially.

In general, conditions which were favorable for good nickel deposition were characterized by a single loop at high frequency, approximately 1000 Hz, with a charge transfer resistance, R_{ct} , of approximately $3 \Omega \text{ cm}^2$, yielding a capacitance of approximately 60 to $70 \mu\text{F cm}^{-2}$. This is illustrated in the spectra, Figure 2, obtained for electrolyte containing $10 \text{ g L}^{-1} \text{ H}_3\text{BO}_3$, $40 \text{ g L}^{-1} \text{ Ni}^{2+}$ and 150 g L^{-1} sodium sulfate at pH 2.5 and 40°C . Conversely, conditions which were very unfavourable for good nickel deposition were characterized by a single, low-frequency loop, usually less than 10 Hz, with a reaction resistance of 1 to $3 \Omega \text{ cm}^2$, resulting in capacitances of 2 to 40 mF cm^{-2} .

A combination of the two capacitive loops was also encountered in many instances (as seen in Figure 3) with the deposit quality determined by the relative size of each loop. As the second, lower frequency loop became more dominant, the deposit quality got progressively worse. In addition, there seemed to be evidence of a diffusion control element, indicated by the 45° slope of the initial part of the second loop. A small inductive loop was present under some conditions, but a specific trend associated with its presence is less clear and more detailed studies are needed in this area.

In general, analysis of data at very low frequencies was difficult. While high frequency data in the EIS tests formed easily definable loops, the lower frequency data

were more difficult to interpret. Depending on the conditions, it was not possible to meaningfully characterize the results from lower frequencies, usually less than about 1 Hz, into capacitive or inductive elements because the data were very irregular. Conditions which yielded better deposits sometimes produced better defined data at low frequencies, but no clear trend was evident. As a result, the significance of these data is unclear, but a more detailed examination of the low frequency region is probably merited. The interpretations presented here utilized the more reproducible higher frequency data, which did present a correlatable trend to deposit morphology.

3.2.1. Effect of nickel concentration

In the absence of H_3BO_3 , the nickel deposits from $40 \text{ g L}^{-1} \text{ Ni}^{2+}$ electrolyte with 150 g L^{-1} sodium sulfate at pH 2.5 and 40°C were considerably degraded. The impedance spectra consisted of a smaller $100 \mu\text{F cm}^{-2}$ loop and a more dominant 26 mF cm^{-2} loop, as seen in Figure 3. Increasing the nickel concentration to $50 \text{ g L}^{-1} \text{ Ni}^{2+}$ improved deposit morphology and shifted the dominant loop to the high frequency region of the spectra, resulting in a spectra which consisted of a $70 \mu\text{F cm}^{-2}$ loop and an 8 mF cm^{-2} loop. Increasing the nickel concentration to $60 \text{ g L}^{-1} \text{ Ni}^{2+}$ further improved the deposit morphology and gave a spectra which consisted of a $70 \mu\text{F cm}^{-2}$ high frequency loop and a small 6 mF cm^{-2} low frequency loop.

3.2.2. Effect of electrolyte pH

A flat, smooth and ductile nickel deposit could be made from electrolyte with $40 \text{ g L}^{-1} \text{ Ni}^{2+}$ electrolyte at 40°C if

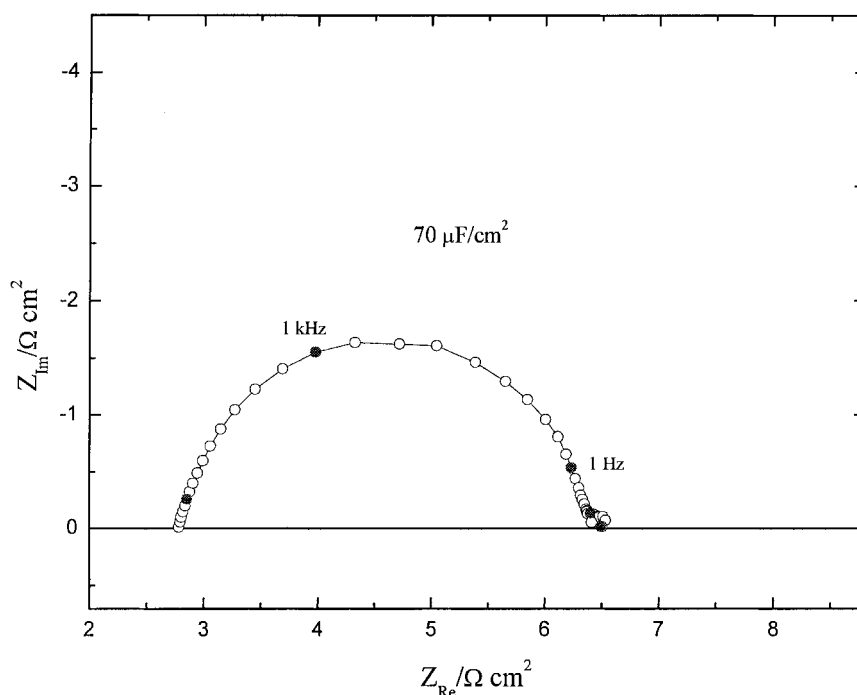


Fig. 2. Complex plane impedance spectra for electrolyte containing $10 \text{ g L}^{-1} \text{ H}_3\text{BO}_3$, $40 \text{ g L}^{-1} \text{ Ni}^{2+}$ and 150 g L^{-1} sodium sulfate at pH 2.5 and 40°C , no stirring, Pt anode, EW-Ni substrate.

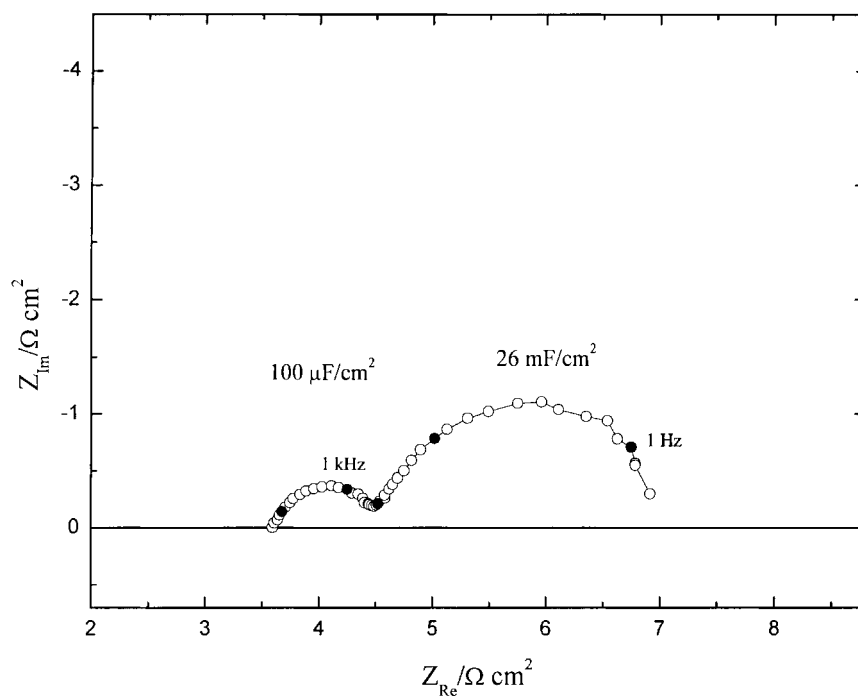


Fig. 3. Complex plane impedance spectra for electrolyte containing $40 \text{ g L}^{-1} \text{ Ni}^{2+}$ and 150 g L^{-1} sodium sulfate at pH 2.5 and 40°C , no stirring, Pt anode, EW-Ni substrate.

the pH was lowered to 2.0, and the corresponding impedance spectra for such conditions consisted of a single $62 \mu\text{F cm}^{-2}$ loop. Conversely, increasing the electrolyte pH to 3.5 resulted in a very bad deposit, and the spectra consisted of the 38 mF cm^{-2} loop shown in Figure 4. The presence of a passivating film and increased diffusion control is very evident in this particular plot.

3.2.3. Effect of electrolyte temperature

Increasing the electrolyte temperature was very effective at improving the deposit morphology quality and the EIS spectra reflected this change. While the spectra for $40 \text{ g L}^{-1} \text{ Ni}^{2+}$ electrolyte at pH 2.5 and 40°C consisted of a $100 \mu\text{F cm}^{-2}$ loop and a 26 mF cm^{-2} loop (Figure 3), the spectra for similar electrolyte at 50°C

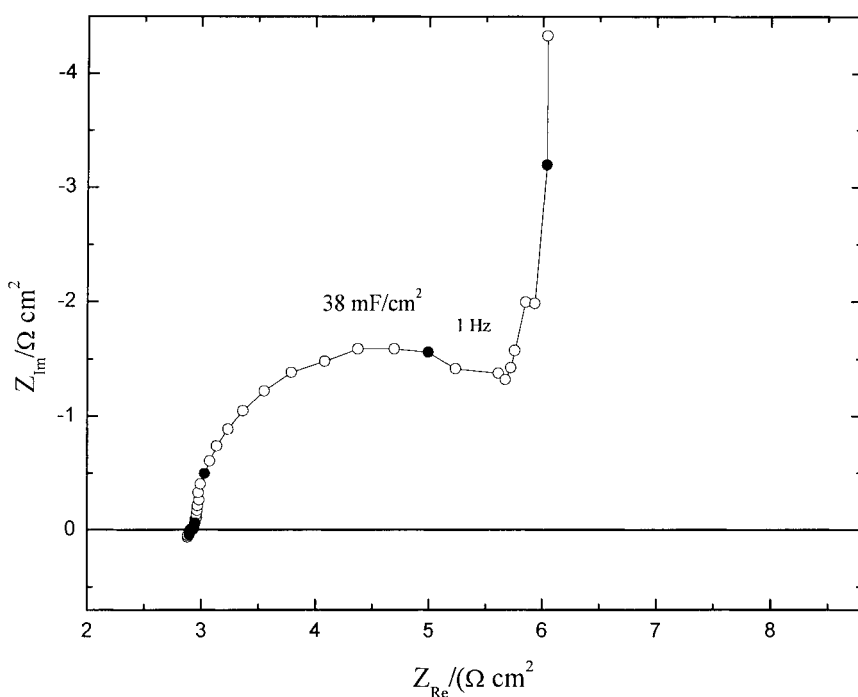


Fig. 4. Complex plane impedance spectra for electrolyte containing $40 \text{ g L}^{-1} \text{ Ni}^{2+}$ and 150 g L^{-1} sodium sulfate at pH 3.5 and 40°C , no stirring, Pt anode, EW-Ni substrate.

had a dominant $60 \mu\text{F cm}^{-2}$ loop and a smaller 6 mF cm^{-2} loop. The spectra given in Figure 5 for similar electrolyte at 60°C consisted of a single $60 \mu\text{F cm}^{-2}$ loop. A very small inductive loop may also be present at low frequencies in the range of 1 Hz . Thus, as deposition conditions improved, the high frequency loop dominated the low frequency loop in the EIS spectra.

The impedance spectra did not change appreciably with either a decrease in the electrolyte pH to 2.0 or an increase in the nickel concentration if the temperature was held constant at 60°C . The spectra for both 50 and $60 \text{ g L}^{-1} \text{ Ni}^{2+}$ electrolyte at 60°C consisted of a single loops with capacitance values of 76 and $64 \mu\text{F cm}^{-2}$, respectively, and the small inductive loop present at about 1 Hz in the latter spectra (Figure 5) is especially prominent.

Although increasing the temperature from 40 to 60°C for pH 3.5 electrolyte improved the deposit morphology, the overall deposit quality was still quite poor. The improved, but still poor, morphology could be predicted based on the impedance spectra. While the spectra for the pH 3.5 electrolyte at 40°C consisted of a single 38 mF cm^{-2} loop, the impedance spectra for the same pH 3.5 electrolyte at 60°C consisted of a $60 \mu\text{F cm}^{-2}$ loop and a smaller 2 mF cm^{-2} loop.

3.2.4. Effect of electrolyte agitation

Stirring the electrolyte was effective at improving the deposit morphology quality, and the EIS continued to be reflective of this change. The spectra for a stirred $40 \text{ g L}^{-1} \text{ Ni}^{2+}$ electrolyte at pH 2.5 and 40°C consisted of a single $70 \mu\text{F cm}^{-2}$ loop. This is another indication that diffusion is an important aspect of the deposition process.

3.2.5. Impedance analysis

One consistent trend among the impedance spectra associating good nickel deposit morphology was the presence of a high-frequency loop of low capacitance, on the order of $60 \mu\text{F cm}^{-2}$. Degraded nickel deposit morphology is associated with the presence of a low-frequency capacitive loop of high capacitance, on the order of a few tens of mF cm^{-2} . Impedance spectra consisting of both a low-capacitance loop and high-capacitance loop indicate that a mixed morphology should be expected. As the deposit morphology improves, the size of the low-capacitance loop increases relative to the high-capacitance loop. A small inductive loop typical of a reaction control [2, 3] appeared with high temperature electrolytes, but only if the first loop dominated the spectra, indicating that the diffusion control had been eliminated.

Unfortunately, there does not appear to be an identifiable correlation to deposit current efficiency and the EIS curves. Electrolytes which gave good deposits at 20 mA cm^{-2} , such as those which contained boric acid, had a pH value of 2.0, a temperature of 60°C , or were stirred all had similar impedance spectra, a single high-frequency loop, but current efficiencies which varied by almost 20%. A more extensive study using a different experimental procedure or methodology may be needed to characterize the hydrogen reduction reaction and relative current efficiency. Of particular importance is the need to clearly identify the role of diffusion in the deposition mechanism.

As proposed by Epelboin et al. [2, 3] the deposition of nickel is thought to occur through two steps; the formation of Ni_{ads}^+ which is subsequently followed by reduction to Ni. The high frequency loop in the

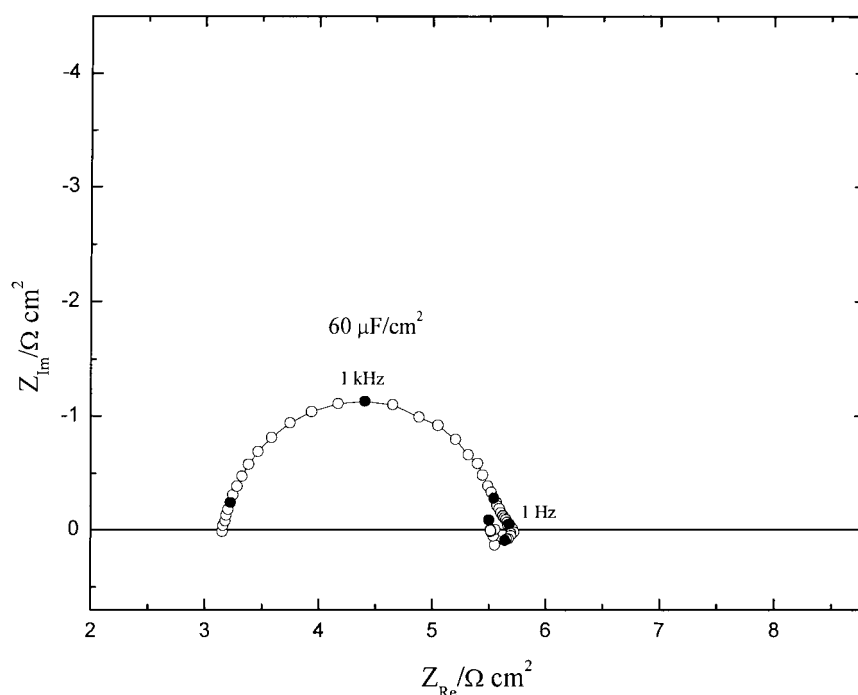


Fig. 5. Complex plane impedance spectra for electrolyte containing $60 \text{ g L}^{-1} \text{ Ni}^{2+}$ and 150 g L^{-1} sodium sulfate at pH 2.5 and 60°C , no stirring, Pt anode, EW-Ni substrate.

impedance spectra is generally attributed to the final metal reduction and both the frequency and capacitance values of the high frequency loops obtained in this study are consistent with those reported in the literature [2–5, 14, 16, 17, 18]. The same studies attribute a low frequency loop, present at a few mHz, to an adsorbed hydrogen film. However, the low frequency loops obtained in this research were on the order of a few Hz, much higher than the range of a few mHz reported by others. This may be due to different electrolyte compositions or test conditions, but the magnitude of the capacitance values obtained at low frequencies in this study, on the order of a few mF cm⁻², are probably too large to be the result of adsorbed hydrogen, which are typically only a few hundred $\mu\text{F cm}^{-2}$ [19]. This indicates that the low frequency loop, and the degraded morphology it indicates, are not the result of adsorbed hydrogen, but rather a more passivating film-forming species.

The frequencies obtained for the low-frequency loops in this study are similar to the frequencies of the inductive loop reported to be caused by the relaxation of the surface coverage by an inhibiting nickel hydroxide species, such as (NiOH)_{ads} [2–5]. The Ni_{ads}⁺ is presumably complexed with hydroxide because the concurrent reduction of hydrogen increases the local OH⁻ concentration. It is more probable that the low-frequency loop present under the conditions of this study indicate an increase in the cathode coverage by an oxidized, passivating nickel species, possibly due to the onset of increased diffusion control of the deposition mechanism. Additionally, the capacitance values of these low-frequency loops are similar in magnitude to those obtained in other systems, such as the formation of a high surface area PbO₂ layer on lead anodes [20]. This suggests the presence of a dominating layer which inhibits the reduction of nickel, or allows the inclusion of partially oxidized nickel particles, resulting in a decrease in deposit quality. The presence of this oxidized film may also be the cause for the presence of oxygen detected by Auger spectroscopy in degraded samples [1].

Under optimal conditions which result in high deposit quality, the reduction reaction appears to be the dominant or rate-controlling step, resulting in good nickel quality and the single low capacitance loop in the impedance spectra. Under nonideal conditions, the formation of a thicker reaction layer of nickel hydroxide inhibits or interferes with nickel reduction, causing degraded nickel deposit quality and the appearance of a high capacitance loop in the impedance spectra. Varying the significant factors such as electrolyte pH, temperature, nickel concentration, etc., presumably changes the stability of the adsorbed film by affecting the transport of ions, solubility of double-layer species and deposition potentials, among other possibilities. The nature of the inductive loop is unclear, but its presence is generally associated with good deposit morphology from high temperature and high pH electrolytes with additives.

4. Conclusions

Electrolytic deposition of nickel from acid sulfate electrolytes with a good physical morphology and high current efficiency can occur under a variety of conditions. Previous work clearly demonstrated the relationship between certain electrolyte parameters and additives to deposit quality. Deposit morphology was favored by high nickel concentration, low pH, high electrolyte temperature and stirring. A low pH and stirring reduced the current efficiency, while high nickel concentration and temperature improved the current efficiency.

A more fundamental influence of these factors on the deposition process was revealed by examination of the electrode reactions via electrochemical impedance spectroscopy. The impedance spectra showed features which related to both the deposit quality and possible shifts in the deposition mechanism. The spectra for good quality nickel deposits consisted of a single, high frequency loop with a capacitance of about 60 $\mu\text{F cm}^{-2}$. As the deposit quality became worse, a second loop appeared at lower frequencies. The characteristics of this loop indicated the onset of a passivating type nickel hydroxide layer, possibly resulting from the onset of diffusion control. Good deposit morphology was associated with the presence of the low capacitance loop, while degraded deposit morphology occurred when an additional reaction mechanism element was present in the EIS plot. As indicated, the second loop is thought to be related to the presence of an oxidized nickel film which can form if hydrogen ion concentration is low. This could occur if H⁺ ion diffusion is insufficient to maintain a low pH in the reaction layer region. Unfortunately, the data from these tests did not give any apparent correlation to process current efficiency and relative hydrogen reduction. A relationship might be found using a different experimental methodology.

The success of the EIS technique indicates that it might be used as a possible sensor technique for deposit quality. Although buffers such as boric acid are effective at ensuring good deposit quality, their use may not be possible in certain electrowinning applications. Controlling the electrodeposition of nickel from an acid sulphate solution then requires a balance of many parameters to achieve optimal physical morphology. By exposing the dominant reaction mechanism, EIS can be used to consistently predict the resultant deposit morphology made using a broad range of electrolyte conditions.

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